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DEVELOPMENT OF NOVEL SPINEL-TYPE MIXED OXIDES TO ACHIEVE CIRCULARITY IN BIO-BASED SORBENTS

Ionela Grecu, Petrisor Samoila, Corneliu Cojocaru, Andra-Cristina Enache

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, 41A Grigore Ghica Vodă Alley, 700487, enache.andra@icmpp.ro, Romania

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Introduction

Environmental pollution poses complex health and socio-economic challenges, particularly in rapidly industrializing regions. The discharge of untreated effluents has led to severe contamination of water bodies, prompting research into scalable and cost-effective purification technologies.

Magnetic nanoparticles, especially spinel ferrites, have emerged as promising candidates due to their chemical stability, high adsorption capacity and catalytic activity, making them suitable for various environmental applications. However, their practical use is limited by intrinsic drawbacks such as particle agglomeration, driven by elevated surface energy and magnetic interactions, which compromise colloidal stability and long-term performance.

To overcome these challenges, strategies to fine-tune magnetic properties and functionality are being explored in the context of sustainable solutions for wastewater treatment technologies.

Materials and methods

Novel spinel ferrites based on Ni-Zn were synthesized via a sol–gel auto-combustion method, by controlled Zn substitution and rare-earth cations doping (La^{3+}, Dy^{3+}, Nd^{3+}), in order to modulate their magnetic properties. Nickel, zinc, iron, and rare-earth nitrates were dissolved in ultrapure water in stoichiometric ratios, followed by the addition of citric acid, as a complexing and fuel agent. The solution was heated to 80 °C to promote chelation, yielding a dark brown gel that underwent self-combustion at ~200 °C and was further treated at 350 °C to ensure complete fuel decomposition. Post-combustion annealing was performed at 500 °C for 5h, 700 °C for 5h, and 900 °C for 7h to remove residual organics and facilitate cation incorporation into the spinel lattice. The resulting product was a fine black powder, indicative of successful ferrite formation.

The newly synthesized ferrites were characterized by Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), and Vibrating Sample Magnetometer (VSM) to assess their structural, morphological, and magnetic properties. Thus, the ferrite exhibiting the highest magnetization was selected for incorporation into chitosan-based beads, with the aim of characterization and testing as adsorbents for organic pollutants from wastewaters.

Results and conclusions

Rare-earth-doped nickel–zinc spinel ferrites with the general formula $Ni_{0.6}Zn_{0.4}Fe_{2-x}RE_xO_4$ (x = 0, 0.02; RE = La, Nd, Dy) were synthesized via the sol–gel auto-combustion method. XRD analysis confirmed the formation of spinel structure, as evidenced by the presence of characteristic diffraction peaks. The recorded infrared spectra, shown in Figure 1, further support the XRD findings by displaying characteristic metal–oxygen vibrational bands. Representative peaks in the 600–400 cm^{-1} range are typical of spinel ferrites, exhibiting two absorption bands, corresponding to M–O bond stretching vibrations at octahedral sites (542–586 cm^{-1}) and tetrahedral sites (397–408 cm^{-1}), indicative of inverse spinel ferrites.

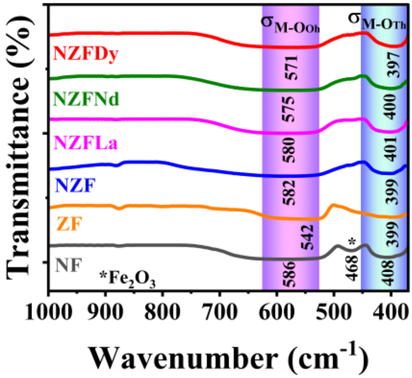

Figure 1. FT-IR spectra of nickel ferrite (NF), zinc ferrite (ZF), nickel–zinc ferrite (NZF), and rare-earth-doped nickel–zinc ferrites (NZFLa, NZFNd, and NZFDy)

TEM analysis revealed well-defined grains with slight agglomeration, likely due to magnetic dipole–dipole interactions. VSM measurements demonstrated superparamagnetic behavior, advantageous for the magnetic recovery and reuse of the ferrite particles. Importantly, the ferrite exhibiting the highest magnetization was intended to be embedded in chitosan-based bio-sorbents for the adsorption of organic pollutants, and its magnetic properties enable the efficient recovery of these polymeric sorbents. Thus, the tunable structural, morphological, and magnetic properties of the synthesized ferrites highlight their potential for the development of magnetically recoverable bio-adsorbents, with uses in removal of persistent pollutants from aqueous media.

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